

What are the problems with the density functional theory?

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From a physical point of view, there is one big problem in density functional theory (DFT) - the fact is that this is a typical “electromagnetic theory” of chemical bonding. Consequently, there will never be exact solutions (“on the tip of a pen”).

Since “...the concept of electron density... answers the question: how likely is it to find an electron inside an infinitely small volume while all other electrons are located anywhere...” [1].

In other words, according to DFT, electron density determines the probability of finding a particular electron within a certain volume, while other electrons have arbitrary positions. That is, there is a clear localization of the chemical bond electron. This contradicts the principle of particle identity, on the basis of which quantum mechanics explains the energy of a chemical bond.

It is worth noting that the classical quantum chemical calculations of a chemical bond proceed from the fact that during the formation of a bond, the electrons are placed so that there is a minimum Coulomb repulsion between them, often schematic diagrams are drawn in textbooks. This approach is a typical manifestation of the “electromagnetic theories” of chemical bonding.

But, according to the principle of particle identity, the electrons of a chemical bond are equivalent and indistinguishable. This is a fundamental point.

Therefore, we will never be able to distinguish and identify a single electron in a chemical bond. Here is a quote from de Broglie from the book “Revolution in Physics” [2]:

“...To show how far we have gone from the old ideas, consider the case of a gas of particles of the same nature, obeying the Pauli principle, for example, an electron gas. According to the exclusion principle, no two electrons of this gas can be in the same state...

Thus, the uncertainty relations forbid talking about the position and state of motion of two particles at the same time.

The very fact that we are talking about the fact that the energy states of the particles are completely determined does not allow us to talk any more about the distance between them, because they are not localized in any way...”.

It is quite obvious that the energy states of the bond electrons are determined, because we know the binding energy exactly. This means that we cannot say anything definite about the position of electrons inside a chemical bond (according to the Heisenberg uncertainty principle).

Since the electrons are delocalized over the entire volume of the chemical bond, they are equivalent and indistinguishable, and fundamentally have no position.

There is only a chemical bond - there are no individual electrons inside a chemical bond and cannot be.

Actually, this is a classical quantum description. For example, in an atom, an electron initially also does not have a specific position (before our experimental definition), everything is similar with a chemical bond.

As a consequence, drawing various diagrams with the attraction-repulsion of electrons and nuclei is a manifestation of typical “electromagnetic theories” of chemical bonding, which attempt to explain the chemical bond on the basis of Coulomb's law.

But, the chemical bond has a quantum nature.

Therefore, the “electromagnetic approach” will only give approximate empirical calculations. And we need an accurate calculation of the chemical bond, and it is possible to do it only taking into account the fact that the chemical bond is of a purely quantum nature.

1. Shklovsky A. G., Beregovoi A. V. The Theory of the Electron Density Functional for Atoms and Simple Molecules. Belgorod, 2014. P. 20.
2. Louis de Broglie. Revolution in Physics. P. 124. Atomizdat, Moscow, 1965 (134 pages).